

Thermal Casimir vs Casimir–Polder forces: Equilibrium and non-equilibrium forces

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We critically discuss whether and under what conditions Lifshitz theory may be used to describe thermal Casimir–Polder forces on atoms or molecules. An exact treatment of the atom–field coupling reveals that for a ground-state atom (molecule), terms associated with virtual-photon absorption lead to a deviation from the traditional Lifshitz result; they are identified as a signature of non-equilibrium dynamics. Even the equilibrium force on a thermalized atom (molecule) may be overestimated when using the ground-state polarizability instead of its thermal counterpart.

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Dispersion forces such as Casimir and Casimir–Polder (CP) forces are of increasing relevance in nanophysics [1]; recent successes include the chemical identification of surface atoms via atomic force microscopy [2] as well as the construction of novel biomimetic dry adhesives [3]. They become important in efforts to miniaturize atom chips [4] and play a key role in experiments placing upper bounds on non-standard gravitational forces [5].

In all of these areas, a thorough understanding of dispersion forces under realistic conditions must account for their temperature dependence induced by thermal photons [6]. A series of high-precision experiments [7] has triggered a renewed interest in this thermal Casimir force [8] by opening the perspective of its experimental investigation [9]. It was noticed that, depending on the model chosen to describe the metal response, Lifshitz theory can yield different answers for the temperature dependence of the Casimir energy between two metal plates [10]. The resulting debate concerning the correct description of the thermal Casimir force [11] will ultimately have to be settled by experiments. Non-equilibrium situations of two plates of different temperatures have recently been suggested as sensitive probes to the quantum electrodynamics (QED) of the Casimir effect [12].

The CP force on single atoms can be measured indirectly via spectroscopic means; clear evidence for thermal frequency shifts has been found for atoms inside a cavity [13] and their signature has been detected in the interaction of atoms with a sapphire surface [14]. The novel non-equilibrium CP forces predicted for the case of different surface and environment temperatures [15] have recently been observed via their effect on the center-of-mass oscillations of a trapped Bose–Einstein condensate [16]. While some theoretical studies of the thermal CP force are based on a QED treatment of the atom–field coupling [17, 18], the vast majority of investigations invokes a macroscopic calculation using Lifshitz theory [6, 19, 20] or a linear-response description of the atom [15, 21] (leading to equivalent results).

The macroscopic approach to the CP force is based on a very close relation between Casimir and CP forces. It

is the validity of this one-to-one correspondence and its results for the CP force that we intend to investigate in this Letter, so let us briefly recount the argument in its traditional form: Generalizing the famous Lifshitz result for two plates [6], the thermal Casimir force on a homogeneous body of arbitrary shape occupying a volume V in free space due to the presence of another body can be given as a Matsubara sum [22, 23]

$$\mathbf{F} = 2k_{\text{B}}T \int_V d^3r \sum_{N=0}^{\infty} \left(1 - \frac{1}{2}\delta_{N0}\right) \times \left[\text{Tr} \left\{ \mathbf{I} \times [\nabla \times \nabla \times + (\xi_N/c)^2] \mathbf{G}^{(1)}(\mathbf{r}, \mathbf{r}', i\xi_N) \times \overleftarrow{\nabla}' \right\}_{\mathbf{r}=\mathbf{r}'} - (\xi_N/c)^2 \nabla \cdot \mathbf{G}^{(1)}(\mathbf{r}, \mathbf{r}, i\xi_N) \right] \quad (1)$$

with Matsubara frequencies $\xi_N = 2\pi k_{\text{B}}TN/\hbar$. Here, $\mathbf{G}^{(1)}$ is the scattering part of the classical Green tensor

$$[\nabla \times \nabla \times - (\omega/c)^2 \varepsilon(\mathbf{r}, \omega)] \mathbf{G}(\mathbf{r}, \mathbf{r}', \omega) = \delta(\mathbf{r} - \mathbf{r}') \quad (2)$$

associated with the bodies that are characterized by their dielectric permittivity $\varepsilon(\mathbf{r}, \omega)$. The result (1) can be obtained from the zero-temperature force by applying the simple replacement rule

$$\frac{\hbar}{\pi} \int_0^{\infty} d\xi f(i\xi) \mapsto 2k_{\text{B}}T \sum_{N=0}^{\infty} \left(1 - \frac{1}{2}\delta_{N0}\right) f(i\xi_N) \quad (3)$$

which is equivalent to replacing the zero-point energy $\frac{1}{2}\hbar\omega$ by a thermal spectrum $[n(\omega) + \frac{1}{2}]\hbar\omega$ with photon number $n(\omega) = 1/[e^{\hbar\omega/(k_{\text{B}}T)} - 1]$. To derive the CP force, one assumes that one body consists of a dilute gas (number density η) of atoms with polarizability $\alpha(\omega)$, so that its permittivity may be approximated by $\varepsilon(\omega) = 1 + \eta\alpha(\omega)/\varepsilon_0$. After a linear expansion in α , it follows that the thermal CP force is given by [22, 23]

$$\mathbf{F}(\mathbf{r}_A) = -\mu_0 k_{\text{B}}T \sum_{N=0}^{\infty} \left(1 - \frac{1}{2}\delta_{N0}\right) \xi_N^2 \alpha(i\xi_N) \times \nabla_A \text{Tr} \mathbf{G}^{(1)}(\mathbf{r}_A, \mathbf{r}_A, i\xi_N). \quad (4)$$

As an immediate consequence of its macroscopic derivation, this force expression is very similar in structure to the respective Casimir force. In particular, the replacement rule (3) is again valid which often serves as a starting point for studies of the thermal CP force [24].

In view of the high precision of modern experiments, the current widespread use of the macroscopic result (4) and the replacement rule (3) for calculating thermal CP forces calls for a critical discussion of their validity. In this Letter we clarify the extent to which Eq. (4) can be used on the basis of a direct calculation of the time-dependent thermal CP force from the atom-field coupling Hamiltonian. We will demonstrate that force components associated with thermal-photon absorption will generically lead to deviations from Eq. (4). As we will show, the macroscopic result provides a reasonable approximation to the force on a fully thermalized atom, provided that the atomic polarizability is correctly interpreted.

In electric dipole approximation, the force on an atom or a molecule (called atomic system in the following) prepared in an incoherent superposition of internal eigenstates $|n\rangle$ is given by [23, 25]

$$\mathbf{F}(\mathbf{r}_A, t) = \langle [\nabla \hat{\mathbf{d}} \cdot \hat{\mathbf{E}}(\mathbf{r})]_{\mathbf{r}=\mathbf{r}_A} \rangle, \quad (5)$$

where it is assumed that the internal and translational motion of the atomic system decouple in the spirit of Born-Oppenheimer approximation. In order to evaluate this expression, one needs to solve the coupled dynamics of the electromagnetic field and the atomic system, which is governed by the Hamiltonian [26]

$$\hat{H} = \int d^3r \int_0^\infty d\omega \hbar\omega \hat{\mathbf{f}}^\dagger(\mathbf{r}, \omega) \cdot \hat{\mathbf{f}}(\mathbf{r}, \omega) + \sum_n E_n \hat{A}_{nn} - \sum_{m,n} \hat{A}_{mn} \mathbf{d}_{mn} \cdot \hat{\mathbf{E}}(\mathbf{r}_A) \quad (6)$$

($\mathbf{d}_{mn} = \langle m | \hat{\mathbf{d}} | n \rangle$, $\hat{A}_{mn} = |m\rangle\langle n|$). The bosonic dynamical variables $\hat{\mathbf{f}}^\dagger$ and $\hat{\mathbf{f}}$, which describe the elementary excitations of the body-assisted electromagnetic field, can be used to construct an expansion of the electric-field operator $\hat{\mathbf{E}}(\mathbf{r}) = \int_0^\infty d\omega \hat{\underline{\mathbf{E}}}(\mathbf{r}, \omega) + \text{H. c.}$ according to

$$\hat{\underline{\mathbf{E}}}(\mathbf{r}, \omega) = i \sqrt{\hbar/(\pi\epsilon_0)} (\omega/c)^2 \int d^3r' \sqrt{\text{Im} \epsilon(\mathbf{r}', \omega)} \times \mathbf{G}(\mathbf{r}, \mathbf{r}', \omega) \cdot \hat{\mathbf{f}}(\mathbf{r}', \omega). \quad (7)$$

The expansion coefficients are given in terms of the classical Green tensor (2) which obeys the integral relation

$$\frac{\omega^2}{c^2} \int d^3s \text{Im} \epsilon(\mathbf{s}, \omega) \mathbf{G}(\mathbf{r}, \mathbf{s}, \omega) \cdot \mathbf{G}^*(\mathbf{s}, \mathbf{r}', \omega) = \text{Im} \mathbf{G}(\mathbf{r}, \mathbf{r}', \omega). \quad (8)$$

The Hamiltonian (6) implies that the atom-field dynamics is governed by the system of equations

$$\dot{\hat{A}}_{mn} = i\omega_{mn} \hat{A}_{mn} + \frac{i}{\hbar} \sum_k (\mathbf{d}_{nk} \hat{A}_{mk} - \mathbf{d}_{km} \hat{A}_{kn}) \cdot \hat{\mathbf{E}}(\mathbf{r}_A), \quad (9)$$

$$\dot{\hat{\mathbf{f}}}(\mathbf{r}, \omega) = -i\omega \hat{\mathbf{f}}(\mathbf{r}, \omega) + \sqrt{\text{Im} \epsilon(\mathbf{r}, \omega)/(\hbar\pi\epsilon_0)} (\omega/c)^2 \times \sum_{m,n} \hat{A}_{mn} \mathbf{d}_{mn} \cdot \mathbf{G}^*(\mathbf{r}_A, \mathbf{r}, \omega). \quad (10)$$

We eliminate the field by formally integrating Eq. (10) and substituting the result back into Eq. (9), which we arrange in normal ordering. After using the integral relation (8), we obtain

$$\dot{\hat{A}}_{mn}(t) = i\omega_{mn} \hat{A}_{mn}(t) + \hat{Z}_{mn}(t) + \frac{i}{\hbar} \sum_k \int_0^\infty d\omega \{ e^{i\omega t} \hat{\underline{\mathbf{E}}}^\dagger(\mathbf{r}_A, \omega) [\mathbf{d}_{nk} \hat{A}_{mk}(t) - \mathbf{d}_{km} \hat{A}_{kn}(t)] + e^{-i\omega t} [\hat{A}_{mk}(t) \mathbf{d}_{nk} - \hat{A}_{kn}(t) \mathbf{d}_{km}] \cdot \hat{\underline{\mathbf{E}}}(\mathbf{r}_A, \omega) \} \quad (11)$$

where

$$\hat{Z}_{mn}(t) = \frac{\mu_0}{\hbar\pi} \sum_{j,k,l} \int_0^\infty d\omega \omega^2 \mathbf{d}_{kl} \cdot \text{Im} \mathbf{G}(\mathbf{r}_A, \mathbf{r}_A, \omega) \int_0^t d\tau \cdot \{ e^{-i\omega(t-\tau)} [\mathbf{d}_{jm} \hat{A}_{jn}(t) - \mathbf{d}_{nj} \hat{A}_{mj}(t)] \hat{A}_{kl}(\tau) + e^{i\omega(t-\tau)} \hat{A}_{kl}(\tau) [\mathbf{d}_{nj} \hat{A}_{mj}(t) - \mathbf{d}_{jm} \hat{A}_{jn}(t)] \} \quad (12)$$

denotes the zero-point contribution to the internal atomic dynamics. The thermal contribution can be determined iteratively by substituting the self-consistent solution

$$\hat{A}_{mn}(t) = e^{i\omega_{mn}t} \hat{A}_{mn} + \frac{i}{\hbar} \sum_k \int_0^\infty d\omega \int_0^t d\tau e^{i\omega_{mn}(t-\tau)} \times [\hat{A}_{mk}(\tau) \mathbf{d}_{nk} - \hat{A}_{kn}(\tau) \mathbf{d}_{km}] \cdot \hat{\underline{\mathbf{E}}}(\mathbf{r}_A, \omega) e^{-i\omega\tau} + \text{H. c.} \quad (13)$$

into the truncated Eq. (11) [without the zero-point contribution $\hat{Z}_{mn}(t)$] back into itself and taking expectation values. With the field initially being prepared in a thermal state $\hat{\rho}_T = \exp[-\hat{H}_F/(k_B T)] / \text{Tr}\{\exp[-\hat{H}_F/(k_B T)]\}$, $\hat{H}_F = \int d^3r \int_0^\infty d\omega \hbar\omega \hat{\mathbf{f}}^\dagger(\mathbf{r}, \omega) \cdot \hat{\mathbf{f}}(\mathbf{r}, \omega)$, the non-vanishing averages of the field operators are

$$\langle \hat{\underline{\mathbf{E}}}^\dagger(\mathbf{r}, \omega) \hat{\underline{\mathbf{E}}}(\mathbf{r}', \omega') \rangle = (\hbar\mu_0/\pi) n(\omega) \omega^2 \text{Im} \mathbf{G}(\mathbf{r}, \mathbf{r}', \omega) \delta(\omega - \omega') \quad (14)$$

[recall Eqs. (7) and (8)]. One thus obtains a closed system of equations for the internal atomic dynamics

$$\langle \dot{\hat{A}}_{mn} \rangle = i\omega_{mn} \langle \hat{A}_{mn} \rangle + \langle \hat{Z}_{mn} \rangle + \langle \hat{T}_{mn} \rangle, \quad (15)$$

with the thermal contribution being given by

$$\begin{aligned} \langle \hat{T}_{mn}(t) \rangle &= \frac{\mu_0}{\hbar\pi} \sum_{k,l} \int_0^\infty d\omega \omega^2 n(\omega) \int_0^t d\tau [e^{-i\omega(t-\tau)} + e^{i\omega(t-\tau)}] \\ &\quad \times \{ e^{i\tilde{\omega}_{mk}(t-\tau)} \mathbf{d}_{nk} \cdot \text{Im } \mathbf{G}(\mathbf{r}_A, \mathbf{r}_A, \omega) \\ &\quad \cdot [\mathbf{d}_{lm} \langle \hat{A}_{lk}(\tau) \rangle - \mathbf{d}_{kl} \langle \hat{A}_{ml}(\tau) \rangle] \\ &\quad + e^{i\tilde{\omega}_{kn}(t-\tau)} \mathbf{d}_{km} \cdot \text{Im } \mathbf{G}(\mathbf{r}_A, \mathbf{r}_A, \omega) \\ &\quad \cdot [\mathbf{d}_{nl} \langle \hat{A}_{kl}(\tau) \rangle - \mathbf{d}_{ln} \langle \hat{A}_{ln}(\tau) \rangle] \}. \end{aligned} \quad (16)$$

For weak atom-field coupling, this system can be solved in Markov approximation using the relations $\langle \hat{A}_{mn}(\tau) \rangle \simeq e^{-i\tilde{\omega}_{mn}(t-\tau)} \langle \hat{A}_{mn}(t) \rangle$ and $\int_0^t d\tau e^{ix(t-\tau)} \simeq \pi\delta(x) + i\mathcal{P}/x$.

For a non-degenerate system, the off-diagonal elements of the atomic density matrix $\hat{\sigma}$ decouple from one another as well as from the diagonal elements, and one finds that the internal atomic dynamics follows the rate equations

$$\dot{\sigma}_{nn}(t) = -\Gamma_n \sigma_{nn}(t) + \sum_k \Gamma_{kn} \sigma_{kk}(t), \quad (17)$$

$$\dot{\sigma}_{mn}(t) = [-i\tilde{\omega}_{mn} - \frac{1}{2}(\Gamma_m + \Gamma_n)] \sigma_{mn}(t), \quad m \neq n \quad (18)$$

($\sigma_{mn} = \langle m | \hat{\sigma} | n \rangle = \langle \hat{A}_{nm} \rangle$). Here, the total loss rates read

$$\begin{aligned} \Gamma_n &= \sum_k \Gamma_{nk} = \frac{2\mu_0}{\hbar} \sum_k \tilde{\omega}_{nk}^2 \{ \Theta(\tilde{\omega}_{nk}) [n(\tilde{\omega}_{nk}) + 1] \\ &\quad + \Theta(\tilde{\omega}_{kn}) n(\tilde{\omega}_{kn}) \} \mathbf{d}_{nk} \cdot \text{Im } \mathbf{G}(\mathbf{r}_A, \mathbf{r}_A, |\tilde{\omega}_{nk}|) \cdot \mathbf{d}_{kn} \end{aligned} \quad (19)$$

and the shifts of the atomic transition frequencies $\tilde{\omega}_{mn} = \omega_{mn} + \delta\omega_m - \delta\omega_n$ are given by

$$\begin{aligned} \delta\omega_n &= \sum_k \delta\omega_{nk} = \frac{\mu_0}{\pi\hbar} \sum_k \mathcal{P} \int_0^\infty d\omega \omega^2 \left[\frac{n(\omega) + 1}{\tilde{\omega}_{nk} - \omega} \right. \\ &\quad \left. + \frac{n(\omega)}{\tilde{\omega}_{nk} + \omega} \right] \mathbf{d}_{nk} \cdot \text{Im } \mathbf{G}(\mathbf{r}_A, \mathbf{r}_A, \omega) \cdot \mathbf{d}_{kn}; \end{aligned} \quad (20)$$

they reduce to the perturbative result derived in Ref. [18] upon setting $\tilde{\omega}_{nk} \simeq \omega_{nk}$ in the denominators.

With these preparations, we evaluate the CP force (5) with the help of Eqs. (7), (13) and (14) and the solution to Eq. (10) as

$$\begin{aligned} \mathbf{F}(\mathbf{r}_A, t) &= \frac{i\mu_0}{\pi} \sum_{n,k} \int_0^\infty d\omega \omega^2 \nabla \mathbf{d}_{nk} \cdot \text{Im } \mathbf{G}^{(1)}(\mathbf{r}, \mathbf{r}_A, \omega) \cdot \mathbf{d}_{kn} \Big|_{\mathbf{r}=\mathbf{r}_A} \\ &\quad \times \int_0^t d\tau \langle \hat{A}_{nn}(\tau) \rangle \{ n(\omega) e^{[i(\omega + \omega_{nk}) - (\Gamma_n + \Gamma_k)/2](t-\tau)} \\ &\quad + [n(\omega) + 1] e^{[-i(\omega - \omega_{nk}) - (\Gamma_n + \Gamma_k)/2](t-\tau)} \} + \text{c. c.} \end{aligned} \quad (21)$$

Here we have used the correlation function

$$\langle \hat{A}_{mn}(t) \hat{A}_{kl}(\tau) \rangle = \delta_{nk} \langle \hat{A}_{ml}(\tau) \rangle e^{[i\tilde{\omega}_{mn} - (\Gamma_m + \Gamma_n)/2](t-\tau)} \quad (22)$$

which follows from Eq. (18) by means of the quantum regression theorem [27]. Evaluating the τ integral in Markov approximation and the ω integral by means of contour-integral techniques (cf. Ref. [25]), one finds that the thermal CP force on an atomic system prepared in an incoherent superposition of energy eigenstates is given by $\mathbf{F}(\mathbf{r}_A, t) = \sum_n \sigma_{nn}(t) \mathbf{F}_n(\mathbf{r}_A)$ with force components

$$\begin{aligned} \mathbf{F}_n(\mathbf{r}_A) &= -\mu_0 k_B T \sum_{N=0}^\infty \left(1 - \frac{1}{2} \delta_{N0} \right) \xi_N^2 \nabla \text{Tr} \{ [\alpha_n(i\xi_N) + \alpha_n(-i\xi_N)] \cdot \mathbf{G}^{(1)}(\mathbf{r}_A, \mathbf{r}, i\xi_N) \} \Big|_{\mathbf{r}=\mathbf{r}_A} \\ &\quad + \mu_0 \sum_k \{ \Theta(\tilde{\omega}_{nk}) \Omega_{nk}^2 \\ &\quad \times [n(\Omega_{nk}) + 1] \nabla \mathbf{d}_{nk} \cdot \mathbf{G}^{(1)}(\mathbf{r}, \mathbf{r}_A, \Omega_{nk}) \cdot \mathbf{d}_{kn} \Big|_{\mathbf{r}=\mathbf{r}_A} - \Theta(\tilde{\omega}_{kn}) \Omega_{kn}^{*2} n(\Omega_{kn}^*) \nabla \mathbf{d}_{nk} \cdot \mathbf{G}^{(1)}(\mathbf{r}, \mathbf{r}_A, \Omega_{kn}^*) \cdot \mathbf{d}_{kn} \Big|_{\mathbf{r}=\mathbf{r}_A} + \text{c.c.} \} \end{aligned} \quad (23)$$

[$\Omega_{nk} = \tilde{\omega}_{nk} + i(\Gamma_n + \Gamma_k)/2$] and atomic/molecular polarizability

$$\alpha_n(\omega) = \frac{1}{\hbar} \sum_k \left[\frac{\mathbf{d}_{nk} \mathbf{d}_{kn}}{-\Omega_{nk} - \omega} + \frac{\mathbf{d}_{kn} \mathbf{d}_{nk}}{-\Omega_{nk}^* + \omega} \right]. \quad (24)$$

This result generalizes the zero-temperature force calcu-

lated in Ref. [25].

In order to compare this force with the macroscopic result (4), we consider an isotropic atomic system in the perturbative limit $\Omega_{nk} \simeq \omega_{nk}$, whereby Eq. (23) simpli-

fies to

$$\begin{aligned} \mathbf{F}_n(\mathbf{r}_A) = & -\mu_0 k_B T \sum_{N=0}^{\infty} \left(1 - \frac{1}{2} \delta_{N0}\right) \\ & \times \xi_N^2 \alpha_n(i\xi_N) \nabla_A \text{Tr} \mathbf{G}^{(1)}(\mathbf{r}_A, \mathbf{r}_A, i\xi_N) \\ & + \frac{\mu_0}{3} \sum_k \omega_{nk}^2 \{ \Theta(\omega_{nk}) [n(\omega_{nk}) + 1] - \Theta(\omega_{kn}) n(\omega_{kn}) \} \\ & \times |\mathbf{d}_{nk}|^2 \nabla_A \text{Tr} \text{Re} \mathbf{G}^{(1)}(\mathbf{r}_A, \mathbf{r}_A, \omega_{nk}) \quad (25) \end{aligned}$$

and coincides with the negative gradient of the frequency shift (20) given in Ref. [18]. In addition to the Matsubara sum, the thermal CP force has resonant contributions proportional to $n(\omega_{nk})$ and $n(\omega_{nk})+1$, respectively, which are due to the absorption and emission of photons by the atomic system. Even the force $\mathbf{F}_0(\mathbf{r}_A)$ on a ground-state atom or molecule exhibits resonant force components $-\frac{1}{3}\mu_0\omega_{k0}^2 n(\omega_{k0}) |\mathbf{d}_{0k}|^2 \nabla_A \text{Tr} \text{Re} \mathbf{G}^{(1)}(\mathbf{r}_A, \mathbf{r}_A, \omega_{k0})$ associated with thermal-photon absorption which lead to a discrepancy with the macroscopic result (4). These resonant forces can be observed on time scales which are short with respect to the inverse ground-state heating rates Γ_{0k}^{-1} , and their magnitude scales with the number of thermal photons at the respective transition frequency $n(\omega_{k0})$. Polar molecules thus present an ideal candidate for studying them, since their heating time can be of the order of several seconds, and the thermal photon number at the relevant vibrational and rotational transition frequencies in the microwave regime can reach values of up to a few hundred at room temperature [28]. As discussed in Ref. [14], the enhanced frequency shifts observed very recently via selective reflection spectroscopy of cesium in the far infrared might be due to a resonant thermal effect of this kind.

Our approach allows us to discuss the full dynamics of the CP force. It is thus able to reveal that resonant force components associated with absorption and stimulated / spontaneous emission of photons are a genuine non-equilibrium effect: According to Eq. (17), the atomic system reaches thermal equilibrium with its environment in the long-time limit and is described by the thermal state $\hat{\sigma}_T = e^{-\sum_n \tilde{E}_n \hat{A}_{nn} / (k_B T)} / \text{Tr}[e^{-\sum_n \tilde{E}_n \hat{A}_{nn} / (k_B T)}]$ ($\tilde{E}_n = E_n + \hbar\delta\omega_n$). In thermal equilibrium, all resonant force components cancel and the force can be written in the form of Eq. (4) only if the atomic polarizability has been identified as the thermal polarizability, $\alpha_T(\omega) = \sum_n \sigma_{T,nn} \alpha_n(\omega)$. In the limit of a single dominant transition, this equilibrium force is smaller than that resulting from Eq. (4) with $\alpha_0(\omega)$ by a factor $r_T = \tanh[\hbar\tilde{\omega}_{10}/(2k_B T)] = [2n(\tilde{\omega}_{10}) + 1]^{-1}$. The force on ground-state atoms, which is dominated by electronic transitions, is insensitive to this effect at room temperature due to the very small thermal photon number: For Rb ($\omega_{10} = 2.37 \times 10^{15} \text{Hz rad}$ [29]), one obtains $r_T = 1 - 1.3 \times 10^{-26}$ at $T = 300 \text{K}$. As in the case of the non-equilibrium force discussed above, a noticeable devi-

ation from the Lifshitz result is to be expected for polar molecules: For CaF, force components associated with vibrational transitions ($\omega_{10} = 1.15 \times 10^{14} \text{Hz rad}$ [30]) are reduced by a factor $r_T = 0.90$, those associated with rotational transitions ($\omega_{10} = 1.32 \times 10^{11} \text{Hz rad}$ [31]) even by a factor $r_T = 0.0017$ —they are thus strongly reduced with respect to the prediction from Lifshitz theory.

In conclusion, a full quantum-mechanical treatment of the atom–field interaction has revealed that the thermal CP force on a ground-state atom or molecule cannot be obtained from a macroscopic calculation while the force on a fully thermalized atom can—provided that one uses its correct finite-temperature polarizability. As shown, the force on thermalized molecules is considerably smaller than suggested by Lifshitz theory. The resonant contributions to the force that occur for a ground-state atom are due to the absorption of thermal photons and manifest a non-equilibrium effect. In particular, they may dominate the thermal CP force on polar molecules, where they present both a considerable limiting factor for the miniaturisation of molecular surface traps and a novel probe to the surface-assisted thermal dynamics of these molecules. The discussion presented here immediately generalizes to scenarios such as those suggested in Ref. [15] where different parts of the environment are held at different temperatures.

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